

# Comment on: Quantitative study of the $f$ occupation in $\text{CeMIn}_5$ and other cerium compounds with hard X-rays

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The valences of cerium dioxide ( $\text{CeO}_2$ ) and cerium fluoride ( $\text{CeF}_4$ ) have long been a subject of controversy. However the controversy is more related to different nomenclature conventions than to different physical interpretations. Indeed, presenting their photoemission and deep core-level spectroscopies results, Kaindl *et al.* conclude: “This approach confirms that  $\text{CeF}_4$  is tetravalent, but does not deny the covalent admixture of  $4f$  character in the valence band.” [1], followed by a later comment “The purpose of our Letter was to provide a simple experimental criterion to distinguish between mixed-valent (metallic) Ce compounds and the wide-gap, tetravalent insulators  $\text{CeF}_4$  and  $\text{CeO}_2$ , which have been and are still classified by several workers as mixed valent.” [2]. In contrary using an Anderson model Kotany *et al.* obtained: “The conclusion of the present paper is as follows:(a) The ground state of  $\text{CeO}_2$  is the mixed valence state where  $4f^0$  and  $4f^1$  configurations are strongly mixed.[...] (c) The  $4f$  level  $\epsilon_f^0$  is near the top of the valence band.” [3] and propose a  $4f$  occupancy of 0.29 for  $\text{CeF}_4$  and 0.5 for  $\text{CeO}_2$  [4], using notably data from Wuilloud *et al.*, who had initially conclude: “A mixed valence can be definitely excluded in  $\text{CeO}_2$ ”[5]. The texts of these authors and other cited within these works, indicate that the term: “valence” is not uniquely defined. For Kaindl *et al.* electrons of  $4f$  character in covalent bond are part of the valence. In contrary for Kotany *et al.* electrons with  $4f^0$  and  $4f^1$  configurations are not part of the valence even if the strong hybridization and energy level  $\epsilon_f^0$  within the valence band indicate an at least partial covalent bond formation.

For cerium we have to differentiate between the occupancy of the purely atomic  $4f$  orbital ( $n_{fO}$ ) and the amount of electrons with  $4f$  character ( $n_{fH}$ ) in hy-

bridized orbitals. Both contributions behave as localized  $4f$  states. Hybridization can come from chemical bonds such as covalent bonds or formation of an electronic band of partial  $4f$  character, in contrary to valence bonds, valence band or ionic bonds, in which the  $4f$  character is lost or extended. With their model Kotany *et al.* can only obtained the total amount of electrons with  $4f$  character ( $n_{fO} + n_{fH}$ ). The model requires a strong hybridization to reproduce the experimental results indicating that more than the purely atomic  $4f$  orbitals are considered. They define the valence of cerium as:  $4 - (n_{fO} + n_{fH})$ . In contrary, experimentally, using susceptibility or a direct interpretation of x-ray photoemission or absorption spectra one directly obtains an approximate value of  $n_{fO}$  and the valence can be defined as all electrons participating in the bonding:  $4 - n_{fO}$ . For  $\text{CeO}_2$  and  $\text{CeF}_4$  the above mentioned literature results indicate that  $n_{fO} \simeq 0$  while  $n_{fH} \simeq 0.5$  or respectively  $n_{fH} \simeq 0.29$ . The valence value depends on its definition. Note that  $n_{fO}$  can take non-integral values with dynamic fluctuations of electrons between the  $4f$  shell and other orbitals of the same atom [6].

The same issue arises when looking at heavy fermions materials such as  $\text{CeCoIn}_5$ . Using an Anderson impurity model, Sundermann *et al.* obtained a total  $4f$  electron count  $n_{fO} + n_{fH} = 0.97$  [7]. In contrary the valence of 3.15 obtained by comparison of x-ray absorption spectra at the M-edge [8] confirms the orbital occupancy obtained at the L-edge  $n_{fO} \simeq 0.85$  [9]. What is remarkable is that both obtained  $4f$  state occupancies ( $n_{fO} + n_{fH}$  and  $n_{fO}$ ) are unmodified between a magnetic system [ $\text{CeRhIn}_5$  in Ref [7] and  $\text{CeCo}(\text{In}_{0.85}\text{Cd}_{0.15})_5$  in Ref. [8]] and the paramagnetic system  $\text{CeCoIn}_5$ . In heavy fermion materials, the occupancy  $n_{fO}$  is the essential ingredient of the mass renormalization via the Kondo lattice, while for  $\text{CeCoIn}_5$  it was recently demonstrated that the magnetism occurs within a band of partial  $4f$  character [8], namely of  $4f$  occupancy  $n_{fH}$ . The absence of variation in both  $n_{fH}$  and  $n_{fO}$  at the antiferromagnetic-paramagnetic transition is an extremely strong result as it demonstrates that the magnetic transition is independent of the Kondo physics. Indeed, the occupancy of the two independent subsets of  $4f$  electrons  $n_{fH}$  and  $n_{fO}$  responsible for magnetism and Kondo correlations is unaffected by the magnetic transition.

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